



Short communication

Highly lithium-ion conductive thio-LISICON thin film processed by low-temperature solution method

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H I G H L I G H T S

- ▶ A low-temperature solution process has been developed to deposit $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ thin film.
- ▶ The $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ thin film has a lithium-ion conductivity of $1.82 \times 10^{-4} \text{ S cm}^{-1}$ at 30°C .
- ▶ The $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ thin film has a lithium-ion transference number of >0.999 .

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In this paper, we report a low-temperature solution method to deposit thio-LISICON, $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ thin film. The low-temperature solution-processed $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ film shows a lithium-ion conductivity of $1.82 \times 10^{-4} \text{ S cm}^{-1}$ at 30°C , an activation energy of 0.42 eV, and a lithium-ion transference number of >0.999 , which might be applicable in thin film all solid state lithium-ion batteries.

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1. Introduction

All-solid-state thin film rechargeable lithium-ion batteries have shown great promise as power sources for micro devices for many years. However, the too low ionic conductivity of the typical electrolyte limits their performance and application field, e.g., lithium phosphorous oxynitride (LiPON , $\text{Li}_{2.9}\text{PO}_{3.3}\text{N}_{0.46}$) commonly used in current thin film batteries shows a conductivity of about $10^{-6} \text{ S cm}^{-1}$ [1–3]. Higher conductive thin film electrolytes are eagerly expected to replace those conventional liquid electrolytes to enable safer, compacter and longer-life batteries. Great efforts have been devoted to the developments of solid state lithium-ion electrolytes. Several oxide-based materials, including perovskite-

type $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ and NASICON-structured $\text{Li}_{1+x}\text{Ti}_{2-x}\text{M}_x(\text{PO}_4)_3$ ($\text{M} = \text{Al, Ga, In, Sc}$), have achieved ionic conductivities up to $10^{-3} \text{ S cm}^{-1}$ at room temperature [4–10]. But they are unstable in contact with elemental lithium due to the facile Ti^{4+} reduction [4–7]. Sulfide-based electrolytes are considered to be a superior type of ionic conductors due to the larger polarizability of S^{2-} [11–14]. An extremely high room temperature lithium-ion conductivity of $1.2 \times 10^{-2} \text{ S cm}^{-1}$ was recently reached in $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ [12], which however is thermodynamically meta-stable [15,16].

The thio-LISICON family, $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$ ($0 < x < 1$), are thermodynamically stable electrolytes, and $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (LGPS) of them showed a very high room temperature ionic conductivity of $2.2 \times 10^{-3} \text{ S cm}^{-1}$, no reaction with lithium metal and no phase transition up to 500°C , which can perfectly be employed as a thin film electrolyte [11]. Excellent electrochemical performances have been demonstrated in all solid state lithium-ion batteries employing it as electrolyte [17–20].

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Unfortunately, this sulfide is highly hygroscopic and very hard to be processed into film by common film-deposition processes like sputtering or pulse laser deposition (PLD), etc. Only one attempt was reported in 2005 by using PLD, which resulted in a film with a room temperature ionic conductivity of $1.7 \times 10^{-4} \text{ S cm}^{-1}$ [21]. But the technique is not suitable for commercial mass production. A low-temperature solution process should be of great interest for the substantial reduction in cost, facility to high throughput, and ability to deposit on various substrates. Herein, LGPS thin film was deposited by an anhydrous hydrazine solution process, which was proved to be a versatile way to deposit high-quality chalcogenide thin films [22–25].

2. Experimental section

2.1. Synthesis

The LGPS powder was synthesized by solid-state reaction (hereafter SSR) of the stoichiometric amount of Li_2S (99.9%, Alfa Aesar, USA), GeS_2 (Homemade) and P_2S_5 (Chemical purity, Sinopharm Chemical Reagent Co. Ltd, China) at 650 °C for 24 h in evacuated sealed silica tubes (<5 Pa argon). GeS_2 was homemade by reaction of stoichiometric Ge (5N, Sinopharm Chemical Reagent Co. Ltd, China) and S (99.9%, Sinopharm Chemical Reagent Co. Ltd, China) at 900 °C for 2 h in evacuated sealed silica tubes (<5 Pa argon).

2.2. Film deposition

Conventionally, hydrazine-based solution process to fabricate chalcogenide thin films usually involves the steps of 1) dissolving binary chalcogenides into anhydrous hydrazine with additional chalcogens, and 2) mixing the binary chalcogenide hydrazine solutions to form a precursor solution. Li_2S and GeS_2 were readily dissolved into anhydrous hydrazine at room temperature with additional sulfur, but P_2S_5 cannot be dissolved with or without sulfur, even at high temperature of over 100 °C. However, LGPS can be dissolved completely into anhydrous hydrazine at room temperature, even without any additional sulfur. This might be relying on adding highly ionic Li^+ into the lattice of P_2S_5 to reduce the overall covalent framework and increase its ionic portion, which helps to achieve the objective. This has expanded the scope of conventional hydrazine-based solution method, and offered a route for the preparation of multinary chalcogenide thin films which contain hard-to-be-dissolved ingredients.

The SSR LGPS powder was completely dissolved in anhydrous hydrazine (freshly distilled from hydrazine hydrate (85%, Sinopharm Chemical Reagent Co. Ltd, China)) to form a transparent colorless solution of 0.2 M at room temperature. Caution: anhydrous hydrazine is highly toxic and should be handled carefully without exposition to either the liquid or the vapor. To evaluate its feasibility as precursor solution for LGPS electrolyte, the hydrazine solvent was removed from the solution under a flow of dry nitrogen at 120 °C, followed by a heat treatment at 240 °C for 2 h under dry nitrogen. The final solution-processed (SP) LGPS powder was pale white.

To prepare the LGPS film, interdigital molybdenum (Mo) electrode coated glass slide was used as substrate (See Supporting information). The LGPS precursor solution was flooded onto the substrate and spin-casted into film at 3500 rpm for 40 s, after a pre-spin at 150 rpm for 3 s. The spin-casted precursor thin film was immediately transferred to a pre-heated hot plate with a temperature of 240 °C and annealed for 30 min. The entire process was performed in a glove box (M. Braun Co., German) with the concentration of O_2 and H_2O maintained under 0.1 ppm.

2.3. Characterization

X-ray diffraction (XRD) patterns of SSR LGPS powder and SP LGPS powder were collected over a powder X-ray diffractometer (D8 FOCUS, Bruker, German) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). Grazing incidence XRD (GIXRD) pattern of SP LGPS film was also obtained over the diffractometer with an incidence angle of 0.05° . The scan speed was set at $4^\circ/\text{min}$ with the accelerating voltage of 40 kV and emission current of 40 mA. The SSR LGPS powder and SP LGPS powder for XRD characterization were premixed with vegetable oil, and SP LGPS film was covered with vegetable oil film under Ar atmosphere to avoid the attack of air moisture.

Chemical stoichiometries of SSR LGPS powder, SP LGPS powder and SP LGPS film were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), their Li, Ge and P contents were measured, and the S contents were calculated accordingly. SSR LGPS powder, SP LGPS powder and SP LGPS film were pre-dissolved in de-ionized water for chemical composition examination.

In order to study its electrical behavior, SP LGPS powder was pelletized (10 mm diameter and 0.6 mm thickness) by cold pressing at 60 MPa, labeled as SP LGPS pellet. Indium plates were attached on both sides of the pellet to serve as current collectors. AC impedance spectra of the pellet were collected over an electrochemical workstation (CHI660C, Shanghai Chen-Hua Instrument Co., Ltd., China) in a temperature range from 30 °C to 210 °C in 30 °C increments and in a frequency range from 0.1 Hz to 0.1 MHz in a dry argon atmosphere. Cooling process for the measurements was chosen to evaluate their ionic conductivities.

Direct current (DC) conductivity measurements were conducted for SP LGPS pellet in a dry argon flow at room temperature, lithium plates were used as nonblocking electrodes and indium plates as blocking electrodes, respectively, with a DC constant voltage of 1 V was applied on the electrodes, to determine its dominant mobile ion and electronic conductivity. The electronic conductivity of SP LGPS film was assessed by DC polarization by applying a constant voltage of 1 V on the molybdenum electrodes.

The electrochemical windows of SP LGPS pellet were evaluated by cyclic voltammetric measurement using the cell configuration of Pt/SP LGPS pellet/Li. A platinum plate was used as a working electrode and a lithium plate as a counter electrode, the scanning rate was set at 1 mV s^{-1} .

The thickness of SP LGPS film was determined to be 126 nm by optical thickness meter (ZST-2000, Shanghai Zousun Optical Instrument Co., Ltd. China).

3. Result and discussion

XRD pattern of SSR LGPS powder was shown in Fig. 1, which was consistent with the published data [11], indicating that it was crystallized in thio-LISICON structure. The chemical composition of SSR LGPS powder was shown in Table 1, as can be seen, the stoichiometry deviation was very small.

The SP LGPS powder did not shown any significant diffraction peaks in the XRD pattern (Fig. 1), which might be resulted from the very low annealing temperature of 240 °C. A small deficiency of phosphorus was detected in chemical composition examination (Table 1), which should be raised from the P_2S_5 high vapor pressure and its volatilization during drying and/or annealing. However, the stoichiometry deviation of SP LGPS powder was acceptable to work as an electrolyte.

AC impedance patterns of SP LGPS pellet were collected by an impedance analyzer in a dry Ar atmosphere. The measurement temperatures were set at regular interval in the range of 30–210 °C,

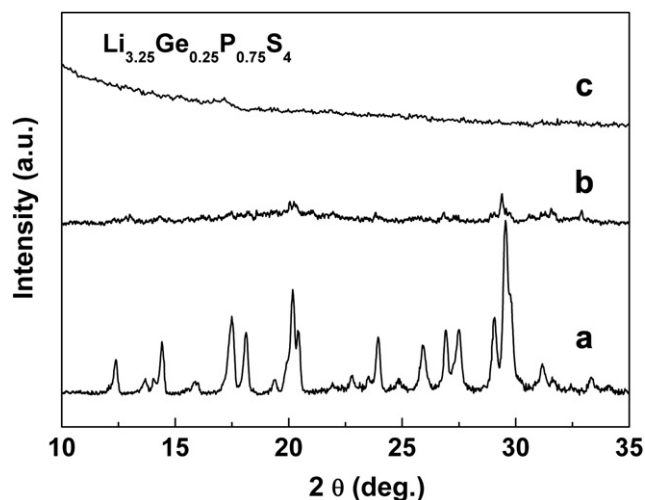


Fig. 1. X-ray diffraction patterns of (a) SSR LGPS powder, (b) SP LGPS powder and (c) grazing incidence X-ray diffraction pattern of LGPS film.

and the frequencies were used ranging from 0.1 Hz to 0.1 MHz. A cooling measurement process was used to evaluate its ionic conductivity. The Nyquist plots of SP LGPS pellet was shown in Fig. 2a, no semicircle was present except for the lowest temperature of 30 °C. Total conductivities were deduced from the Nyquist plots, with an ionic conductivity of $1.13 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C (Fig. 2b). The ionic conductivity was over one order of magnitude lower than the highest reported value ($2.2 \times 10^{-3} \text{ S cm}^{-1}$). Reasons for the lower ionic conductivity might be that SP LGPS pellet was deviated off the best stoichiometry and much poorer crystallized. Perfect linear relation was observed in reciprocal temperature dependence of the logarithmic total conductivities, indicating the pure ionic conductive feature of SP LGPS pellet.

The activation energy of E_a of SP LGPS was calculated over a temperature range of 30–210 °C using the following formula:

$$\sigma_T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

Where σ_T is the total conductivity of the composite electrolyte at the definite temperature, σ_0 is the pre-exponential parameter, k is the Boltzmann constant and T is the Kelvin temperature.

The E_a of LGPS was calculated to be about 0.42 eV (Fig. 2b), which is much higher than the reported data (0.21 eV), and this also might be caused by the sample's stoichiometry deviation and poor crystalline nature.

Fig. 3 shows the results of DC polarization measurement of SP LGPS pellet. When lithium plates were used as electrodes (unblocking electrodes), an almost constant current of $4.5 \times 10^{-4} \text{ A}$ was observed. The DC conductivity was calculated to be $3.4 \times 10^{-5} \text{ S cm}^{-1}$, which was a bit lower than the value

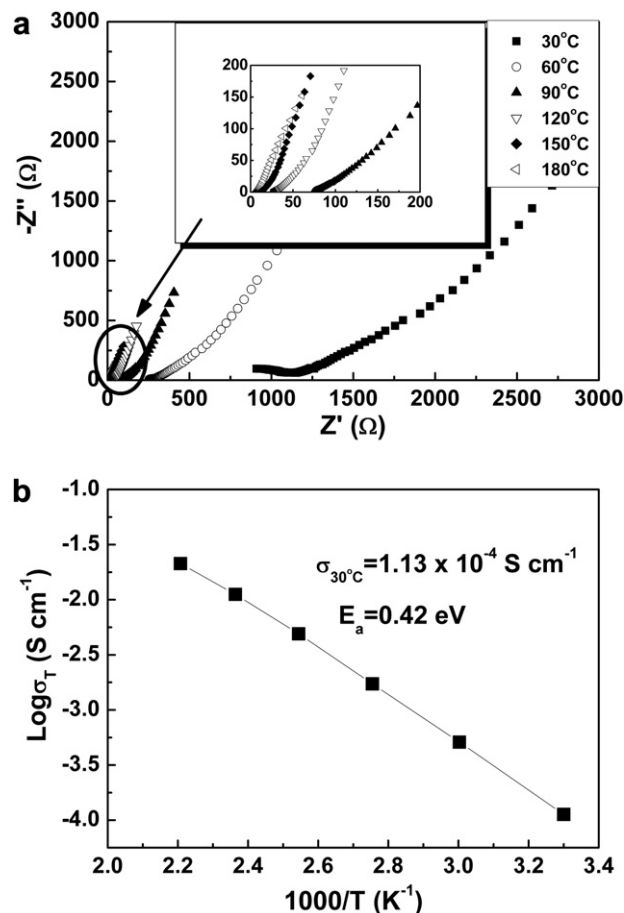


Fig. 2. (a) Impedance spectra for SP LGPS pellet collected at temperatures ranging from 30 °C to 210 °C. (b) Arrhenius plot for the lithium-ion conductivity of SP LGPS pellet.

($1.13 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C) obtained from the impedance measurement using indium plates as electrodes (blocking electrodes). This should be caused by the fact that the actual room temperature was a bit lower than 30 °C when conducting the dc measurement. When using indium electrodes (blocking electrodes), the DC current initially decreased sharply and then stabilized at $2.4 \times 10^{-6} \text{ A}$ after 600 s. The DC conductivity was calculated to be $1.8 \times 10^{-7} \text{ S cm}^{-1}$, over 2 orders of magnitude lower than the

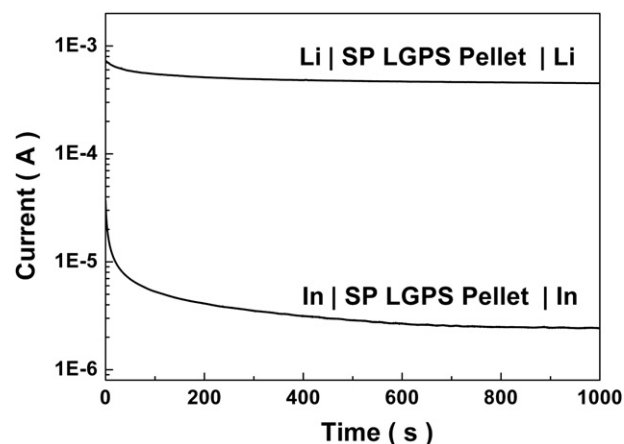


Fig. 3. Time dependence of dc conductivity for SP LGPS pellet derived from currents after applying a constant voltage of 1.0 V.

Table 1
Chemical compositions of SSR LGPS, SP LGPS and LGPS film measured by IPC-AES, the content of S was calculated.

Sample		Li	Ge	P	S (calc.)
SSR LGPS	Mass ratio (%)	11.63	9.35	12.23	66.79
	Atomic ratio	3.25	0.25	0.77	4.05
SP LGPS	Mass ratio (%)	12.43	9.48	11.43	66.66
	Atomic ratio	3.43	0.25	0.71	3.98
LGPS film	Mass ratio (%)	12.42	9.48	11.44	66.66
	Atomic ratio	3.43	0.25	0.71	3.98

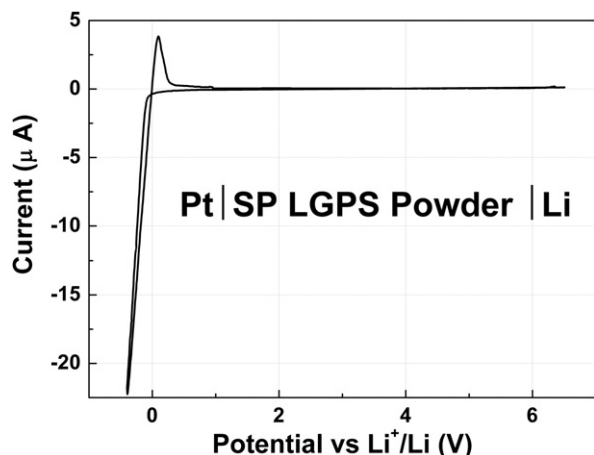


Fig. 4. Cyclic voltammogram of the cell, Li/SP LGPS pellet/Pt.

value obtained by using lithium electrodes. Therefore, the lithium-ion transfer number of SP LGPS pellet is higher than 0.99.

The electrochemical stability of SP LGPS pellet was characterized by cyclic voltammogram (Fig. 4). No significant current peaks were observed within the whole scan range, except for that due to cathodic and anodic lithium deposition/dissolution reactions near 0 V versus Li^+/Li . Since no significant decomposition current was observed, SP LGPS pellet was stable up to 6.5 V, satisfactory for practical application.

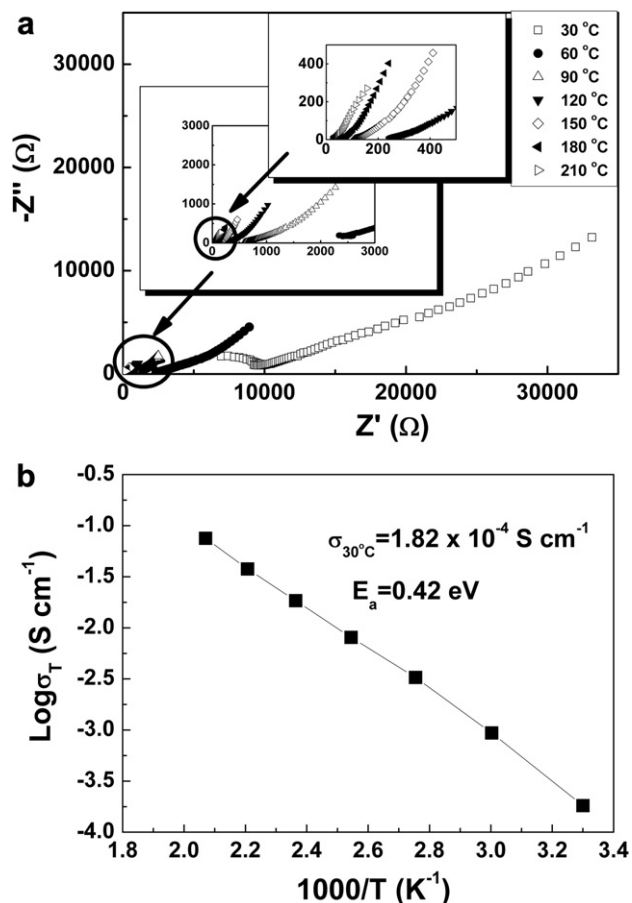


Fig. 5. (a) Impedance spectra for LGPS film collected at temperatures ranging from 30 °C to 210 °C. (b) Arrhenius plot for the lithium-ion conductivity of LGPS film.

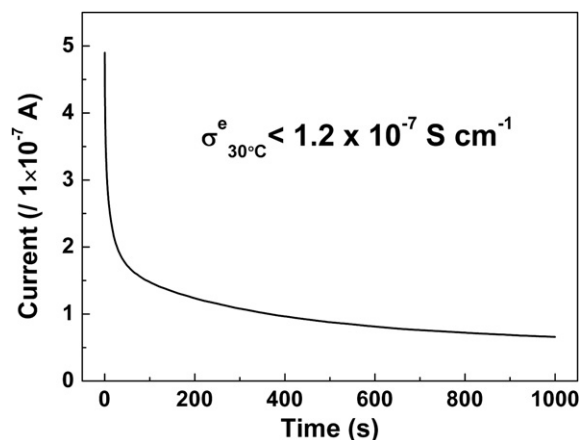


Fig. 6. Time dependence of dc current for LGPS film after applying a constant voltage of 1 V on the electrodes.

As can be seen from above, the LGPS hydrazine solution can be readily used as precursor solution to the targeted LGPS electrolyte, and it can be deposited into films by kinds of non-vacuum liquid techniques. Here we employed the spin-coating method, which was convenient and widely available.

The GIXRD pattern of SP LGPS film shows no intense diffraction peaks. Two reasons might be accounted for this fact, one is that the film was rather poorly crystallized, and the other may be that the film for GIXRD characterization was covered by a vegetable oil film. Similar to SP LGPS powder, a little phosphorus was missing in the film also due to the P_2S_5 volatilization (Table 1). AC impedance spectra for the LGPS film were collected over the temperature range of 30–210 °C in 30 °C increments to assess its ionic conductivity. The impedance plots were mainly composed of sloping diffusion tails in the low frequency region, semicircles in the high frequency range were mainly absent, except for the lowest temperature of 30 °C (Fig. 5a). Total conductivities were deduced from the Nyquist plots, and a value of $1.82 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C was attained, which was a bit higher than that of SP LGPS pellet. This might be ascribed to the denser of the film than the pellet. The conductivity was nearly equivalent to that of PLD processed one, but substantially higher than that of LiPON [1–3,21]. Perfect linear relation was observed in reciprocal temperature dependence of the logarithmic total conductivities. An activation energy of E_a was also measured to be 0.42 eV (Fig. 5b). A negligible electronic conductivity less than $1.2 \times 10^{-7} \text{ S cm}^{-1}$ at 30 °C was detected by dc polarization technique (Fig. 6), which is almost three orders of magnitude lower than the corresponding total conductivity. Therefore, a very high lithium-ion transference number of >0.999 was reached.

The electrochemical stability of LGPS film cannot be evaluated directly at the moment, as we cannot fabricate a reliable lithium electrode over the LGPS film. However, the electrochemical window of LGPS film should be as wide as SP LGPS, as they were fabricated by the same precursor solution and have experienced the same heat treatment.

4. Conclusions

A low-temperature solution process has been successfully developed to deposit LGPS film. The ionic conductivity of the film was $1.82 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C, the activation energy was 0.42 eV, and the lithium-ion transference number was higher than 0.999. The ionic conductivity was over one order of magnitude lower than the highest reported value of bulk LGPS materials. The sharp

decrement in ionic conductivity was mainly considered to be caused by the film's stoichiometry deviation and poor crystalline nature. The solution method might be applicable for coating LGPS thin films onto porous lithium-ion battery electrodes to form effective electrode–electrolyte interfaces in all solid state batteries [26,27].

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2012.09.097>.

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